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14. ABSTRACT
This award was used to acquire a J.A. Woollam Infrared Variable Angle Spectroscopic Ellipsometer (IR-VASE). The IR-VASE unit is capable of obtaining crucial IR information of ultrathin films whilst being complemented with ellipsometry data. This powerful and versatile instrument is the most accurate for optically characterizing surfaces in the infrared spectrum. It provides accurate optical constants, film thickness, chemical information, semiconductor doping levels, and phonon absorption spectra. It has the capability to study liquid/solid interfaces,

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Report Title

Final Report: Acquisition of Infrared Variable Angle Spectroscopic Ellipsometer (IR-VASE)

ABSTRACT

This award was used to acquire a J.A. Woollam Infrared Variable Angle Spectroscopic Ellipsometer (IR-VASE). The IR-VASE unit is capable of obtaining crucial IR information of ultrathin films whilst being complemented with ellipsometry data. This powerful and versatile instrument is the most accurate for optically characterizing surfaces in the infrared spectrum. It provides accurate optical constants, film thickness, chemical information, semiconductor doping levels, and phonon absorption spectra. It has the capability to study liquid/solid interfaces, common in both biology and chemistry applications. Moreover, a thermal stage was acquired to enable characterization in a wide variety of environmental conditions. The installation of the system at the Center for Nanostructured Characterization was completed in October 2015. The IR-VASE will support research in nanotechnology, materials science and engineering, and bioengineering from the Departments of Chemical, General, and Mechanical Engineering, and Chemistry as well.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Almodovar J.*; “Engineering biopolymeric nano materials for tissue engineering applications” Poster presented at the Institute for Functional Nanomaterials External Advisory Board Meeting in Rio Piedras, PR. March 2016

Quiñonez B.*, Castilla D., Almodóvar J.; “Polysaccharide-based polyelectrolyte multilayers: Physicochemical characterization and in vitro studies” Poster presented at the UPRM’s Department of Biology Annual Symposium in Mayaguez, PR. April 2016

Quiñonez B.*, Castilla D., Almodóvar J.; “Polysaccharide-based polyelectrolyte multilayers: Physicochemical characterization and in vitro studies” Paper presented at the 6th Annual Research Symposium of the Asociacion de Estudiantes de Medicina de Puerto Rico in San Juan, PR. April 2016

Quiñonez B.*, Castilla D., Almodóvar J.; “Polysaccharide-based polyelectrolyte multilayers: Physicochemical characterization and in vitro studies” Poster presented at the XXI Sigma Xi Poster Day at UPRM in Mayaguez, PR. April 2016

Quiñonez B.*, Castilla D., Almodóvar J.; “Polysaccharide-based polyelectrolyte multilayers: Physicochemical characterization and in vitro studies” Paper presented at the 2016 Junior Technical Meeting (JTM) and the Puerto Rico Interdisciplinary Meeting (PRISM) in Ponce, PR. March 2016

Number of Presentations: 5.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received	Paper

TOTAL:

Number of Manuscripts:

Books

Received	Book

TOTAL:

Received	Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

Graduate Students

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:...... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):...... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:...... 0.00

Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

NAME

Total Number:

Names of other research staff

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See Attachment

Technology Transfer

Summary

The IR-VASE unit was installed on October 2015 at the University of Puerto Rico Mayaguez's (UPRM) Center for Nanostructured Characterization (CENAC). A basic 2 day training was performed by J.A Wollam during the installation period. Funds from award were used to purchase the IR-VASE unit (Fig 1C), the thermal stage and controllers (Fig 1F), the purge-gas generator (Fig 1B), the translational stage (Fig 1C), and an oil-free compressor (Fig 1A). A constant flow of clean, oil-free, dry, and CO_2 free air is required for the operation and maintenance of the IR-VASE due to the sensitive hydroscopic optics. UPRM provided funding to purchase a dehumidifier (Fig 1B) and completed the funding to purchase the battery back-ups to protect the compressor (Fig 1D) and the IR-VASE (Fig 1E). Battery back-ups were purchased to protect the equipment from the constant variation in voltage and power outages. Day-to-day operation of the CENAC is performed by Mr. Daniel Narvaez, a full time instrumentation technician with ample experience in several characterization techniques, including infrared. Mr. Narvaez, is in charge of operating, maintaining, and training users of the IR-VASE. He preforms daily maintenance checks (Fig 2) to ensure that the IR-VASE is running optimally. He also maintains the user log (Fig 2). Mr. Narvaez will attend an advanced training on IR-VASE data processing on November 2016. This training was included in the IR-VASE purchase.

Figure 1 A) Oil-free compressor to provide clean air to the IR-VASE. B) Purge-gas generator and dehumidifier. C) IR-VASE unit with translational stage. D) Surge protector and battery back-up for the compressor. E) Surge protector and battery back-up for the IR-VASE. F) INSTEC heating stage and controllers.

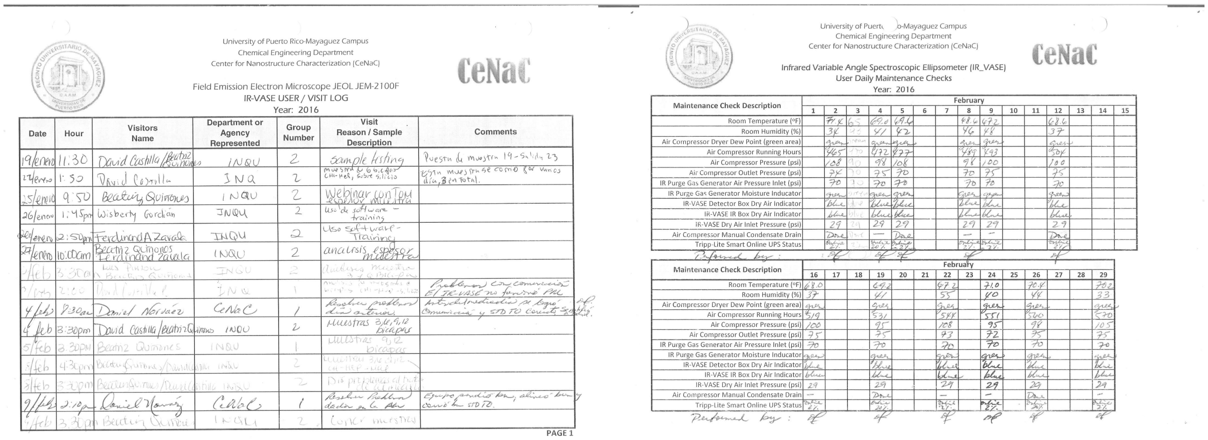

Figure 2 Example of IR-VASE's user-log (left) and maintenance check log (right).

The acquisition of the IR-VASE is fundamental to support research and educational endeavors in the fields of bio/nanomaterials, polymer physics, surface chemistry, and materials engineering at UPRM. Seven research projects of faculty members from the Departments of Chemical Engineering, Mechanical Engineering, General Engineering, and Chemistry at UPRM will directly benefit from the acquisition. These ongoing projects require complete optical characterization of a range of surfaces in the fields of polymer nanostructures, protein/material interactions, surface modifications, thin-film biomaterials, and nanocomposites. Based on this base user group it is estimated that more than 9 graduate students, 15 undergraduate students, and 2 high school students, will benefit immediately from the acquisition of the IR-VASE. The IR-VASE, will allow room for expansion of research interests and collaboration with other researchers interested in optically characterizing surfaces in the infrared spectrum.

The projects that have priority in the use of the equipment are:

1. Biopolymeric Nano-Films for Regenerative Medicine Applications (Jorge Almodovar, Department of Chemical Engineering).
2. Design of Innovative Electrochemical Biosensors (Enrique Melendez, Department of Chemistry).
3. Novel Block Copolymers for Organic Photovoltatic Devices (David Suleiman, Department of Chemical Engineering)
4. Composite Liquid Crystalline Elastomers for Smart Sensing Applications (Aldo Acevedo, Department of Chemical Engineering; and Barbara Calcagno, Department of General Engineering)
5. The Role of Mechanical Stimulus on Collagen Expression During Bone Repair (Paul Sundaram, Department of Mechanical Engineering)
6. Monitoring Amyloidal Fibrilization Confined in Hydrogels (Madeline Torres-Lugo, Department of Chemical Engineering)
7. Biosensor Design for Detection of Vascular Endothelial Growth Factor Levels in Blood Plasma (Elsie I. Pares-Matos, Department of Chemistry; and Pedro J. Resto, Department of Mechanical Engineering).

Summary of on-going tests

Biopolymeric Nano-Films for Regenerative Medicine Applications (Jorge Almodóvar, Department of Chemical Engineering)

In this project, nano-thin films are evaluated as carriers of therapeutics for regenerative medicine applications. These films are constructed using the layer-by-layer (LbL) method. During the LbL assembly, polyelectrolytes are absorbed sequentially on a charged substrate (Fig 3). In this work, we investigate the use of the polysaccharides chitosan and heparin as the polycation and polyanion, respectively. LbL films were constructed on silicon surfaces modified with an anchoring layer of polyethylenimine. Films were constructed to contain 3 and 6 bilayers. IR-VASE was used to evaluate film chemistry and film thickness.

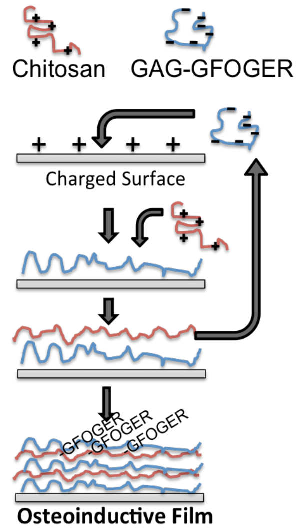

Figure 3 LbL assembly schematic

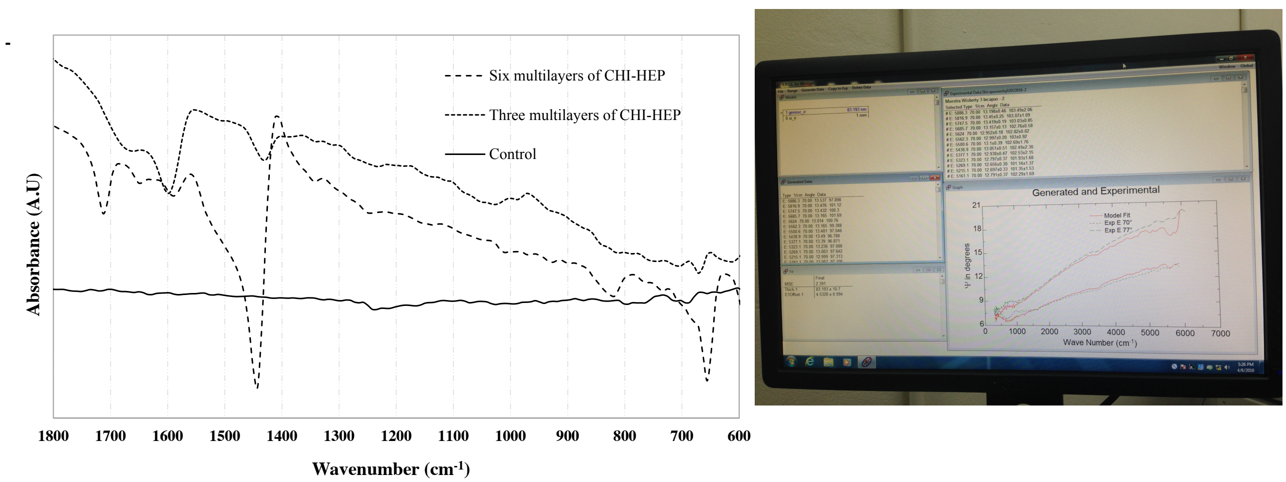

Figure 4 (Left) IR Spectrum of chitosan(CHI)-heparin(HEP) multilayers. Six bilayers (thickness = 209 nm), three bilayers (thickness = 110 nm) and control (silicon surfaces). **(Right)** Screenshot demonstrating an example of the model fitting procedure to obtain film thickness.

Figure 4 shows the IR spectra of the six and three bilayers chitosan-heparin LbL films, along with a pristine silicon control. The characteristic peaks of both polysaccharides are present including the amide I (1733 cm^{-1} - 1600 cm^{-1}) and amide II (1600 cm^{-1} - 1500 cm^{-1}) peaks, as well as heparin's strong sulfate peak around 650 cm^{-1}. We observe that the intensity of the IR signal greatly increases with increasing number of layers. This due to the increase in material absorbed. The versatility of the IR-VASE allows the combination of highly sensitive FTIR with ellipsometry. Thus, by performing fitting of the experimental IR data with pre-defined models we can obtain highly accurate film thickness information (Fig 4). For the analyzed samples, their thicknesses were 209 nm and 110 nm for six and three bilayers, respectively.

Detailed description of equipment purchased with award

Description	**Price**
IR-VASE® Mark II Infrared Variable Angle Spectroscopic Ellipsometer Spectral Range: 1.7 to 30 microns (333 to 5880 cm^{-1}) This is a complete turn-key system, including: · Patented Rotating Compensator (RCE) design · High precision goniometer stage with auto-angle from 31° to 90° · Vertical sample mount with vacuum stage · Operator Computer: Dell Optiplex, i7-3770 processor, Windows 7 Professional, 500GB HD, 4GB RAM, DVDRW, 19inch Monitor, Office 2013 Home and Business. Minimum specifications, subject to change without notice. · WVASE software for data analysis (3 copies). Includes PDF manual and 1 print manual. · 2 day on-site installation and training · Purge Gas Generator to convert compressed air to dry air	$176,000
Manual Sample Translation · 45x45 mm XY	$5,500
INSTEC Heat Stage · Temperature range: -70°C to 600°C · Sample size: up to 0.8" by 0.8" · Includes temperature controller and thermocouple built into the sample chuck to monitor sample temperature. · Enclosure restricts measurements at only 70° angle of incidence, variable angle capability without enclosure. · Active Cooling with Liquid Nitrogen. Dewar and pump included, customer supplies liquid N2. · Software control of temperature to coordinate VASE measurements with temperature profiles. · Enclosure with optical windows allows sample purge. · One full set of IR windows (2) is included. Standard window material is ZnSe, which limits upper wavelength range to about 16-22 microns.	$24,750
100% Oil Free Rotary Dry Scroll Air-Cooled Compressor	$10,632
Materials for electrical connection of compressor	$50.39
Materials for connecting compressed air to IR-VASE	$189.06
Tripplite Smart Online 208/240 & 120V 6KVA, 5.4 kW, Double Conversion UPS Battery Backup*	$2,265.55
Total	**$219,387**

*Total cost of the battery backup was $5275. The difference in cost was covered by UPRM.